

**HIGHLY HYDRATED SULFATE SALTS AS SPECTRAL ANALOGS TO DISRUPTED TERRAINS ON EUROPA.**

J.B. Dalton<sup>1</sup>, C.S. Jamieson<sup>2</sup>, R.C. Quinn<sup>3</sup>, O. Prieto-Ballesteros<sup>4</sup> and J. Kargel<sup>5</sup>, <sup>1</sup>SETI Institute, MS 245-3, NASA Ames Research Center, Moffett Field, CA 94035-1000 email: dalton@mail.arc.nasa.gov, <sup>2</sup>University of Hawaii, Manoa, 2545 McCarthy Hall, Honolulu, HI 96822-2275. email: csjamieso@hawaii.edu. <sup>3</sup>SETI Institute, MS 239-12, NASA Ames Research Center, Moffett Field, CA 94035-1000 email: rquinn@mail.arc.nasa.gov. <sup>4</sup>Centro de Astrobiología, (CSIC/INTA), Torrejón de Ardoz, Madrid (España) e-mail: prietobo@inta.es. <sup>5</sup>Astrogeology Team, U.S. Geological Survey, 2255 N. Gemini Dr., Flagstaff, AZ 86001 e-mail: jkargel@usgs.gov.

**Introduction:** Asymmetric and distorted near-infrared absorption features indicate the presence of hydrated materials on the surface of Europa [1,2]. A number of species have been proposed as the material which plays host to the waters of hydration. The most promising class of these may well be the ones which retain high numbers of water molecules. Earlier work [2,3] has shown discrepancies between near-infrared spectra of disrupted terrains on Europa gathered by the Galileo NIMS instrument and the spectral behavior of hydrated salts of low hydration states. Other work [4,5,6,7] indicates that these discrepancies are reduced at higher levels of hydration. Here we report additional laboratory measurements which strengthen the case for highly hydrated materials on Europa.

**Europa Compared to Water Ice:** Figure 1 depicts the spectrum of dark plains units on the trailing hemisphere of Europa compared to a spectrum of ordinary water ice. The primary water absorption features near 1.0, 1.25, 1.5 and 2.0 microns ( $\mu\text{m}$ ) are shifted and distorted in the Europa spectrum. The broad absorptions near 1.5 and 2.0  $\mu\text{m}$  in the water ice spectrum are composed of several smaller absorptions which combine to produce the broader features. Narrower absorptions such as the crystalline water ice absorption feature at 1.65  $\mu\text{m}$  can be discerned in the Europa spectrum, particularly between 1.5 and 2.0  $\mu\text{m}$ .

**Absorption features of hydrated salts:** Note also the well-rounded shoulders at the right of the 1.0- and 1.25- $\mu\text{m}$  features in the water ice and Europa spectra of Figure 1. These are affected by minor absorptions in the hydrated salt spectra of Figure 2. Many of the minor absorptions become more pronounced in the hydrates because the host molecule obstructs the interactions between individual  $\text{H}_2\text{O}$  molecules which cause molecular vibrations to occur over a broader frequency range. At low temperatures such as those found on the icy satellites, further reduction in interaction between energy states results in enhanced separation of these spectral features [2,6,9]. This effect is subdued in molecules of higher hydration state because the increased number of water molecules are able to interact more directly.

**Effect of Increasing Hydration:** Epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) displays the asymmetric absorption

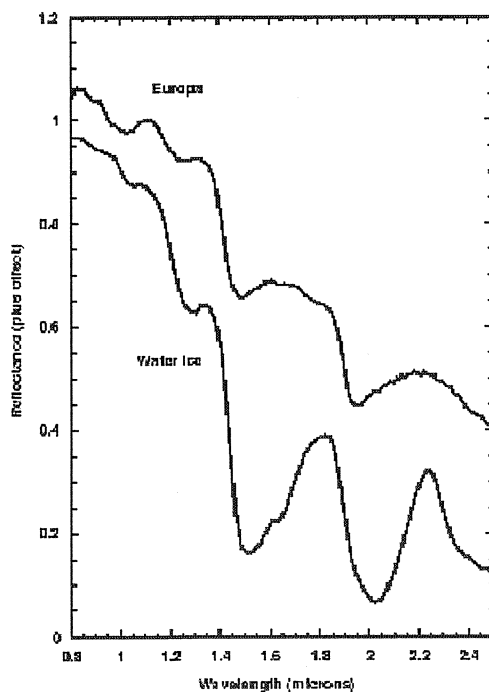
features endemic to the hydrates. However, it contains a number of additional features not seen on Europa. Sodium sulfide monohydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) has broader absorption at 2.0 microns due to the greater number of water molecules, but the orientation of the hydrated waters about the sulfide gives rise to several absorptions at very different energies than those seen in the sulfate hydrates; note the center positions of the 1.5- and 2.0- $\mu\text{m}$  absorptions as compared to the sulfate hydrates. Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) begins to more closely approximate the Europa feature shapes, but again exhibits additional features, notably at 1.75 and 2.2  $\mu\text{m}$ .

**Magnesium Sulfate Dodecahydrate:** We have successfully synthesized magnesium sulfate dodecahydrate ( $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ ) using a compressed-helium cryostat with programmable temperature controller at NASA-Ames Research Center. We began with a mixture of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ , in stoichiometric proportions, which was placed in the environment chamber under dry nitrogen atmosphere. The temperature was programmed to oscillate about the eutectic and peritectic of the 3-phase system with a gradually decreasing amplitude over 16 hours. Each cycle resulted in solvation of a higher proportion of  $\text{H}_2\text{O}$ , until the entire mixture had become dodecahydrate. The identity has been verified using differential scanning calorimetry. Because the dodecahydrate decomposes at temperatures above  $\sim 267$  K, the sample was maintained at subfreezing temperatures using a liquid nitrogen bath during transfer to the calorimeter. A spectrum of the dodecahydrate is shown in Figure 2. The absorption features at 1.5 and 2.0  $\mu\text{m}$  display the same asymmetry as the Europa features, with fewer additional absorptions as seen in the lower hydration state samples. However, as with the other hydrates, a cation-OH stretch at 1.35  $\mu\text{m}$  [8] is apparent cutting into the shoulder of the transition between the 1.25- and 1.5- $\mu\text{m}$  bands, in contrast to the well-rounded shoulders seen in the Europa and water ice spectra.

**$\text{MgSO}_4$  and  $\text{Na}_2\text{CO}_3$  Brines:** When sufficient water is present to create a brine, many of these small spectral features become subdued [7]. This is partly due to the interactions between the numerous water molecules, and partly due to scattering between salt

and water grains within the frozen brine mixture [2]. However, the additional water also tends to broaden the 2.0- $\mu\text{m}$  and deepen the 1.65- $\mu\text{m}$  features, while failing to completely eliminate the 1.35- $\mu\text{m}$  cation-OH stretch. Flash-freezing of brines or other solutions limits crystal growth times, creating many small crystals which act as scattering centers. These scattering centers can decrease spectral contrast, reducing the influence of individual spectral features [2,9].

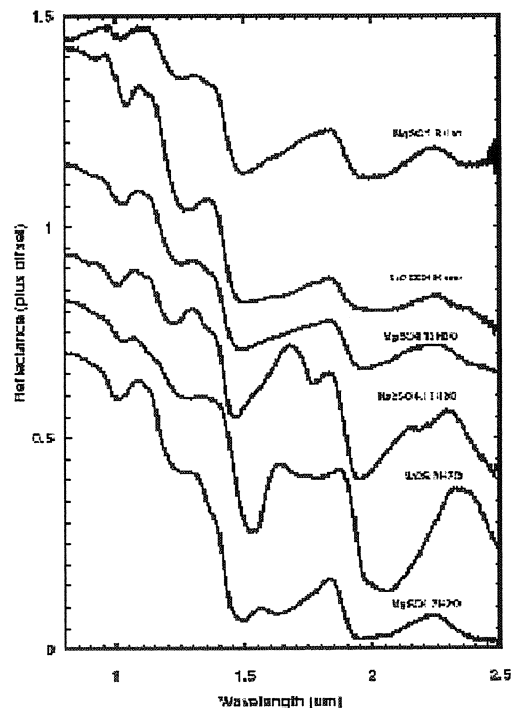
**Mixtures:** While no single material has yet provided a satisfactory match to the Europa spectrum, none have been conclusively ruled out on the basis of spectral arguments, either, and several may be present in low abundances. Neglecting stability considerations, many of these materials could be present at 5 to 60 percent levels by weight. A mixture of several materials with coincident features at 1.5 and 2.0  $\mu\text{m}$  could produce a spectral match without any one material contributing a strong enough absorption to contradict the NIMS data. While this has been tried with limited success using materials of low hydration state [1,2,3], new spectral measurements of highly hydrated materials [4,5] offer the potential to significantly improve upon these earlier studies.



**Figure 1.** Galileo NIMS spectrum of dark terrain on Europa compared to water ice. Europa spectrum is from observation C3ENLINEA and represents a 26-pixel average. The water ice spectrum contains 1-5  $\mu\text{m}$  quartz crystals as neutral scattering elements.

**Conclusions:** As the number of waters of hydration increases, the near-infrared spectra of hydrated salt compounds begin to more closely approximate the Galileo NIMS results. Magnesium sulfate dodecahydrate exhibits uncannily close yet imperfect similarities to the NIMS observations. Discrepancies remaining in the fine structure of brine and hydrate spectra (such as at 1.35  $\mu\text{m}$ ) could be exploited by a properly designed instrument to determine not only the materials, but also the relative proportions of materials, that make up the surface layer. Further laboratory measurements of as-yet unexamined compounds in the hydrate family may reveal even better correspondences.

**References:** [1] McCord, T.B. *et al.* (1998) *Science*, 280, 1242-1245. [2] Dalton, J.B. (2000) Ph.D. Dissertation, Univ. Colo., Boulder. [3] McCord T.B. *et al.* (1999) *JGR*, 104, 11,824-11,852. [4] Carlson R.W. *et al.* (2002) *Icarus* 157, 456-463. [5] Prieto-Ballesteros, O. *et al.* (1999) *LPS XXX*, Abstract #1762. [6] Dalton, J.B. (2003) *Astrobiology*, 3, v. 4. (in press). [7] McCord, T.B. *et al.* (2002) *JGR*, 107, 4-1, 4-6. [8] Dalton, J.B. and Clark R.N. (1999) *LPS XXX*, Abstract #2064. [9] Dalton, J.B. and Clark R.N. (1998) *Bull. Am. Astron. Soc.*, 30, 1081.



**Figure 2.** Spectra of highly hydrated compounds and frozen brines. From bottom: Epsomite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 100K; Sodium sulfide nonahydrate,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , 200K; Mirabilite,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , 200K; Dodecahydrate,  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ , 250K;  $\text{NaHCO}_3$  and  $\text{MgSO}_4$  saturated brines, flash-frozen at 77K.